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Low-voltage electrowetting on a lipid bilayer formed on hafnium oxide¹

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We present a class of electrowetting systems in which lipid bilayers function as reversibly wettable dielectrics, eliminating the need for solid organic dielectrics (e.g. fluoropolymers) in electrowetting systems. These bilayers form spontaneously between water drops and hafnium oxide surfaces in oil and can withstand high electric fields, enabling high contact angle changes at unprecedentedly low voltages. We demonstrate that under well-defined conditions, these electrowetting systems are virtually free of contact angle saturation with low oil-water surface energies ($<1 \text{ mJ/m}^2$), allowing for a reversible contact angle change from over 140° to under 10° using less than 1 V actuation.

Electrowetting, or the electrical manipulation of liquid contact angles on solid surfaces, finds use in a variety of microfluidic applications, including liquid displays [1-3], liquid lenses [4-6], and miniaturized bioassays [7-8]. The development of reliable, low-voltage electrowetting systems is essential for realizing portable electrowetting devices. However, low breakdown fields in organic fluoropolymer dielectrics, which are found in virtually all electrowetting systems, necessitate thick dielectric layers and high operating voltages, typically exceeding 10 V [9-10]. Here we report the development of electrowetting systems that do not contain solid organic dielectrics such as fluoropolymers, but instead contain thin oil-based liquid bilayers with high capacitances per area. Spontaneously formed in the presence of appropriate surfactants, these bilayers facilitate high contact angle changes at low voltages, comparable to those observed in mercury/oil/water electrocapillary systems without dielectric layers [11].

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Electrowetting alters the contact angle of a liquid drop on a solid surface via voltage application across the solid-liquid interface. A typical electrowetting configuration consists of a water drop on a dielectric stack covering a planar electrode, as shown in Fig. 1(a). The Lippmann-Young equation predicts the contact angle change in response to voltage [10]:

$$\cos\theta(V) = \cos\theta_1 + \frac{CV^2}{2\gamma_{w0}} \quad (1)$$

where $\theta(V)$ is the contact angle of the water drop as a function of voltage, θ_1 is the angle at zero voltage (known as Young's angle), C is the capacitance per area of the dielectric, V is the voltage applied between the electrode and the water drop, and γ_{w0} is the surface energy between the water and the nonconductive ambient phase, commonly air or oil. At very short distances (<1 nm), the equation contains an additional term, due to van der Waals forces [12]. However, the van der Waals forces are negligible for these electrowetting systems.

The top surface of the dielectric must be hydrophobic to prevent pinning (irreversible wetting) of the drop on the dielectric surface. Most electrowetting systems contain spin-coated amorphous fluoropolymers such as Teflon AF™ or Cytop™ on top of inorganic dielectrics to obtain reversible wetting [13-16]. Although fluoropolymers enable reversible wetting, their electrical properties—low permittivities and low breakdown fields—render them poor dielectrics [17-18]. Electrical breakdown of the fluoropolymer irreparably damages the electrowetting properties of the system, even if the inorganic dielectrics beneath the fluoropolymer remain intact. Thick fluoropolymer films are required to reduce the electric field and prevent dielectric breakdown of the fluoropolymer, resulting in high actuation voltages for electrowetting.

Here we present an electrowetting system that exhibits the high breakdown field and high capacitance of inorganic dielectrics as well as the hydrophobicity and reversible wettability of

fluoropolymers. This system contains a hafnium oxide dielectric submersed in dodecane containing sorbitan trioleate, a nonionic, lipophilic surfactant. When a water drop is deposited onto the hafnium oxide, sorbitan trioleate adsorbs at the oil-water and oil-hafnium oxide interfaces, forming a lipid bilayer. The disjoining pressure of the bilayer buffers the water from the hafnium oxide. Surfactant bilayers are commonly used to stabilize water-in-oil emulsions [19-20] and have even been used to electrowet two water drops against each other [ref]; however, this effect has never been exploited for electrowetting a water drop on a solid, hydrophilic dielectric surface. The bilayer does not fracture into smaller droplets upon electrowetting, as has been observed for oil films trapped between aqueous drops and fluoropolymer dielectrics [20]. In addition to hydrodynamically trapped oil, a thin layer of oil may also adsorb onto fluoropolymers in water/oil/fluoropolymer systems, due to the van der Waals interactions of these materials [21]. However, these thin films negligibly contribute to the overall capacitance of the system and have not been experimentally quantified. Conversely, the bilayers described here are electrically detectable, functioning as dielectrics at frequencies above 20 Hz. They display interesting liquid dielectric properties, such as pressure-dependent thickness and some ability to self-heal after electrical damage. Stable bilayers are formed with a minimum concentration of 0.1 wt% sorbitan trioleate in dodecane. The resulting oil-water surface energies are low (4 mJ/m^2) compared to most existing electrowetting systems. Interestingly, water drops pin to silicon dioxide and silicon nitride surfaces in the same oil ambient. Water drops even have some tendency to pin to hafnium oxide films that were deposited months earlier, though the pinning is eliminated if the sorbitan trioleate concentration is increased to around 1.0 wt%. If a water drop is placed on hafnium oxide in air and then immersed in dodecane containing sorbitan trioleate, the water drop initially remains attached to the hafnium oxide with a hydrophilic contact angle, though the contact angle slowly increases over the course of days. Conversely, the Young's angle of a water drop dispensed within the oil ambient onto hafnium oxide, as done in our experiments, is $>160^\circ$. This behavior strongly suggests that sorbitan

trioleate adsorbs at both the oil-water and the oil-hafnium oxide interfaces and forms a bilayer, depicted in Fig. 3(a).

For these experiments, the hafnium oxide was deposited onto the silicon electrode via thermal atomic layer deposition (ALD) using tetrakis ethylmethylamino hafnium (TEMAH) and water in an Oxford Instrument OpAL ALD system. 100 cycles of TEMAH dose/ N_2 purge/ H_2O dose/ N_2 purge for 2 s/7 s/0.1 s/8 s were performed at 300°C. The TEMAH precursor was held at 80°C and delivered using 300 sccm Ar carrier gas. The hafnium oxide film was not used in electrowetting experiments until a week after its deposition, allowing the film to equilibrate with ambient conditions. Ellipsometry measurements indicated that the resulting hafnium oxide film was approximately 9 nm thick. The dielectric constant for the film measured approximately 17.

To characterize the electrowetting behavior, a degenerately boron doped single crystal silicon electrode coated with a 9 nm hafnium oxide dielectric was submersed in dodecane containing sorbitan trioleate, and a water drop (~3-4 mm diameter) was deposited on the hafnium oxide surface (Figure 1a). A platinum electrode contacted the water drop, and a voltage was applied to the water drop while the silicon remained grounded. Applied voltage in the form of an AC sine wave from V to $-V$ at 300 Hz was incremented from 0 V to a maximum voltage (forward sweep), resulting in wetting, and then decremented back to 0 V (reverse sweep), resulting in dewetting. The water drop contact angle (θ), the capacitance between the grounded substrate and the water drop (C), and the diameter of the contact area between the water drop and the hafnium oxide were recorded for each applied voltage. The system was allowed approximately 60-90 seconds to equilibrate at each applied voltage before measurements were recorded. The calculated settling times indicate that hydrodynamic equilibrium is reached approximately 60 seconds between each voltage point, given the peak voltage change, drop diameters, bilayer thicknesses, and oil viscosity.

Figure 1(b) shows the electrowetting behaviors of two systems containing hafnium oxide/lipid bilayer dielectrics. Electrowetting systems typically exhibit contact angle saturation, where the contact angle reaches a lower limit and does not decrease any further, or very little, despite an increase in applied voltage. There are a variety of proposed mechanisms for saturation, yet the phenomenon is not well understood and appears to depend on the individual material components in the system [22-24]. The partial wetting system displayed in Fig. 1(b) exhibited contact angle saturation around 115°, whereas the complete wetting system showed virtually no saturation; as captured in Fig. 2.

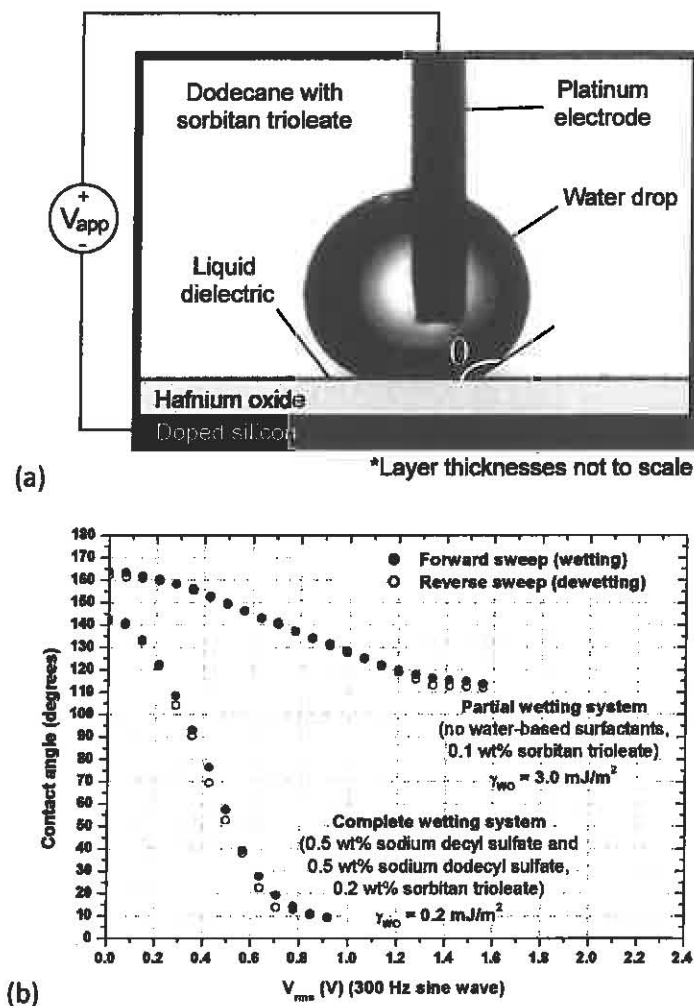


FIG. 1. (a) Configuration for electrowetting on hafnium oxide with a lipid bilayer. A silicon electrode with a hafnium oxide film is immersed in dodecane with sorbitan trioleate. A water drop is placed on the hafnium oxide and contacted by a platinum electrode. A voltage is applied across the hafnium oxide

dielectric and a spontaneously formed lipid bilayer. (b) Electrowetting behavior of two systems containing bilayers. The partial wetting system consisted of a 0.1 N NaCl water drop, a dodecane ambient with 0.1 wt% sorbitan trioleate, and a 9-nm hafnium oxide dielectric. The complete wetting system, though otherwise identical to the partial wetting system, contained additional surfactants in the water drop (0.5 wt% sodium decyl sulfate and 0.5 wt% sodium dodecyl sulfate) and 0.2 wt% sorbitan trioleate in the dodecane. The partial wetting system reached contact angle saturation around 115°, whereas the complete wetting system, which has a lower γ_{wo} , transitioned from 142° to 9°.

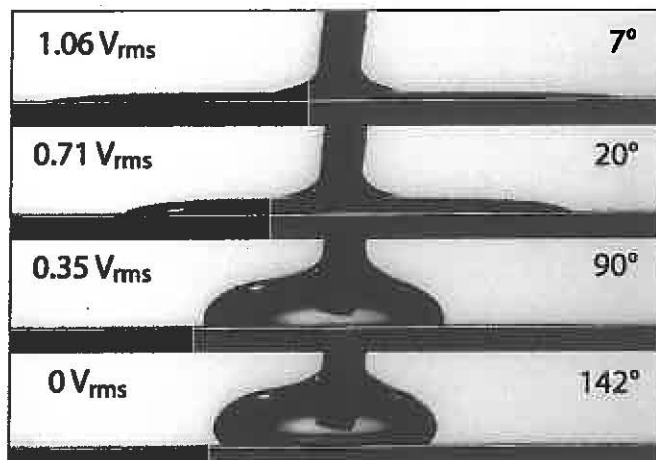


FIG. 2. Images of the complete wetting system at different applied voltages. Images were taken in order of decreasing voltage (from top to bottom chronologically). The contact angle fully restores to the Young's angle ($\sim 142^\circ$) at 0 V after the drop is electrowetted below 10° at 1.06 V.

The capacitance per area of a 0.1 N NaCl water drop on the hafnium oxide film measures higher in air (without the bilayer) than in dodecane with sorbitan trioleate. Accounting for the difference between these two capacitances, the effective thickness of the bilayer can be estimated by modeling the hafnium oxide and the lipid bilayer as two capacitances in series, as shown in Fig. 3(a). For the partial wetting system, the capacitance per area (C_{oil}) and the effective thickness (T_{oil}) of the bilayer in response to applied voltage are plotted in Fig. 3(b). The capacitance per area increased with applied voltage, indicating that the bilayer thinned as the drop was electrowetted. Reducing the voltage increases the thickness of the bilayer again, indicating that the equilibrium thickness is governed by a

balance between the electrostatic pressure P_{elec} (exerted by the applied electric field) and the disjoining pressure Π (arising from the repulsion between the sorbitan trioleate-coated water and hafnium oxide surfaces). In equilibrium, these forces are equal and opposite, assuming that the hydrostatic pressure is negligibly small. P_{elec} can be directly measured using the capacitance per area of the bilayer (C_{oil}) and the hafnium oxide in air (C_{HfO_2}) at different applied voltages (V):

$$P_{elec} = \frac{1}{2\epsilon_0 \epsilon_{oil}} \left(\frac{C_{oil} C_{HfO_2} V}{C_{oil} + C_{HfO_2}} \right)^2 \quad (3)$$

where ϵ_0 is the permittivity of vacuum, ϵ_{oil} is the relative permittivity of dodecane. The theoretical Π from the bilayer can be calculated using the following model for disjoining pressure between two densely packed polymer brushes [25]:

$$\Pi(x) = k_B T \Gamma^{3/2} \left[\left(\frac{h_0}{x} \right)^{9/4} - \left(\frac{x}{h_0} \right)^{3/4} \right] \quad (4)$$

where k_B is the Boltzmann constant, T is the temperature, Γ is the surface density of the molecules at the interface, h_0 is the height of the polymer brush, and x is the distance between the two layers in the bilayer. Taking T_{oil} as the distance x , the disjoining pressure in bilayer can be approximated for different applied voltages. Figure 3(c) compares the magnitudes of the theoretically-determined Π using the polymer brush model and the experimentally obtained P_{elec} for two electrowetting systems containing different concentrations of sorbitan trioleate. For both systems, P_{elec} and Π show remarkably similar behavior for the measured bilayer thicknesses. The best-fit values for Γ used to generate the Π curves in Fig. 3(c) are 2.0×10^{17} molecules/m² for 0.1 wt% sorbitan trioleate and 1.7×10^{17} molecules/m² for 1 wt% sorbitan trioleate. The best-fit values for h_0 for 0.1 wt% and 1 wt% sorbitan trioleate are 1.98 nm and 2.45 nm, respectively. These values are close to the chain length of the sorbitan trioleate molecules

(~2.75 nm). The variations in R_0 and Γ between the two sorbitan trioleate concentrations may be related to their morphology at the interface and are under further investigation.

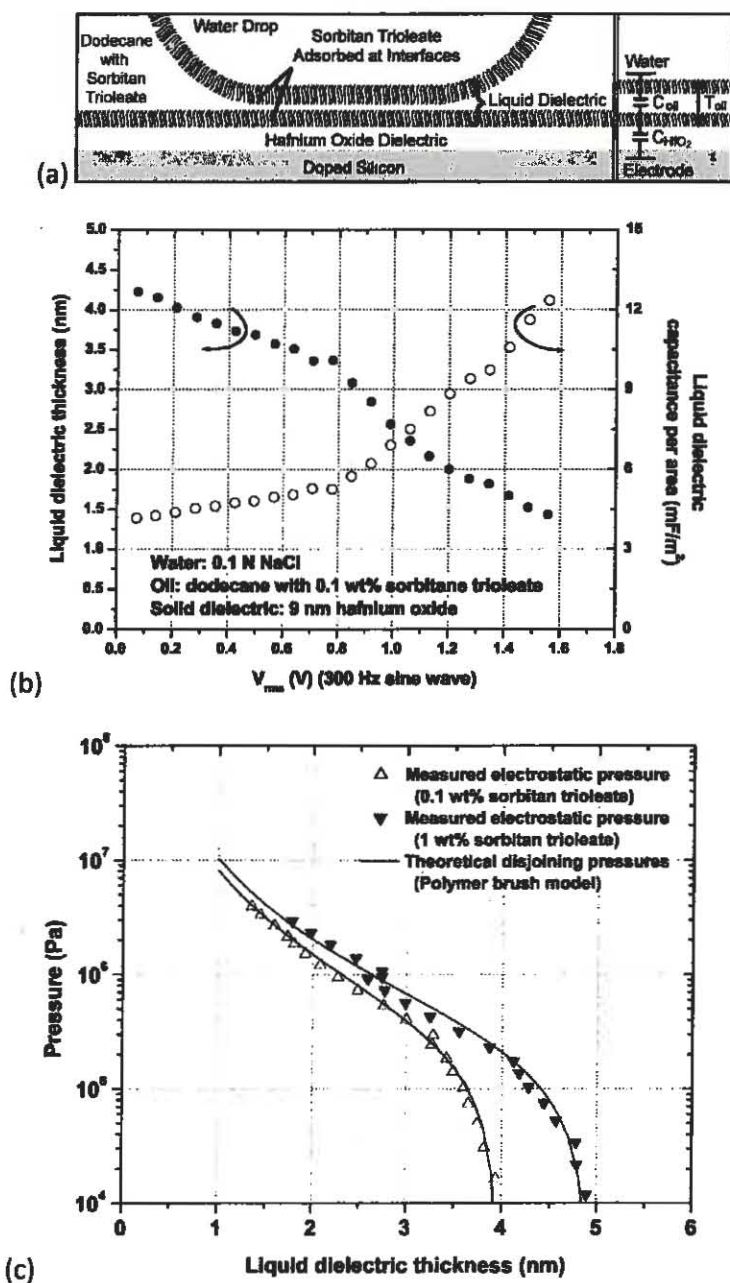


FIG. 3. (a) Schematic depicting the lipid bilayer, which prevents pinning of the water drop to the hafnium oxide. (b) Capacitance per area and effective bilayer thickness versus voltage for the partial wetting system. The bilayer thickness decreases as the voltage increases, indicating a thinning of the oil layer as the drop electrowets. (c) Measured electrostatic pressures and theoretical disjoining pressures versus bilayer thickness in electrowetting systems containing different concentrations of sorbitan trioleate. The

electrostatic pressure was calculated using Eq. 3, and the theoretical disjoining pressure was calculated using a densely packed polymer brush model (eq. 4).

We have demonstrated reversible electrowetting on a high-capacitance dielectric stack consisting of a hafnium oxide film and a self-forming lipid bilayer, eliminating the need for fluoropolymer dielectrics, which have poor electric properties. These systems enable reversible electrowetting across a wide range of contact angles at extremely low voltages. The largest observed contact angle range spanned from over 140° at 0 V to nearly complete wetting ($<10^\circ$) with less than 1 V.

Stable bilayers only form when the concentration of sorbitan trioleate exceeds a threshold (0.1 wt% in dodecane). The resulting oil-water surface energies are quite low and are thus undesirable for most electrowetting applications. However, this reported technique of replacing the fluoropolymer dielectric with a self-healing, high-capacitance, lipid bilayer extends the possibilities for future developments in low-voltage electrowetting technology.

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